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The Permanganates of Magnesium
Zinc and Cadmium.

Dissertation.

Submitted to the Board of University Studies
of the Johns Hopkins University for the
Degree of Doctor of Philosophy.

By
Harold Chambliss

1900.

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A desire to improve the my application of instruction receives from
J. C. Clark, J. H. Henshaw, and Dr. Henshaw

The Permanganates of Magnesium Zinc and Cadmium

Introduction

In 1849 Morse and Olsen (Am. Chem. J. 23, 5, 1131) devised a method for the preparation of permanganic acid by the electrolysis of potassium permanganate. The method as improved by them is capable of yielding the acid in any desired quantity, with practically free of the potassium permanganate and quite free of other impurities.

The successful investigation of a method for preparing the permanganic acid naturally suggested the preparation and study of the metallic salts of the acid - most of which, if they have not been prepared before have not been purified and studied in a detailed way.

In 1873 Martenson (Zinnberich. 1873 254)

for identification purposes reduced the zinc permanganate by treating silver permanganate with zinc chloride. The silver permanganate he has prepared by treating potassium permanganate with silver nitrate. The zinc chloride he used in the reaction with silver permanganate was prepared pure by treating zinc sulphide with barium chloride.

He then describes zinc permanganate as having a red brown shiny and metallic appearance - easily soluble in water when deliquescent in moist air. On heating in a glass tube he found the salt to give purple vapors there remaining in the tube as a porous mass of steel lustre. If the salt, he says, be heated in

Stannous Chloride with some traces of
beautiful blue and yellow ring shaped
formations which he did not investi-
gate. The water solution of the
fine permanganate is free of for-
eign material with stands for
long time without decomposition.
But only a trace of chlorine will de-
compose it gradually (Bull. Soc. Ch. '87-105)

Klobb (Bull. Soc. Ch. de Paris 887, 105) refers
to the preparation of zinc permanganate
by treating with zinc chloride the
permanganate of barium. After
evaporating the solution to a pasty
consistency he crystallized the salt
over phosphorus pentoxide.

His description of the salt agrees with
that of Martenson - he seems however
to have study^{ied} it further than

Shaller, 1891, 92. It states that at 100°C. the salt loses only four molecules of water of crystallization and when heating to the sixth molecule the salt was wholly decomposed according to the following equation:



Lebb studied this reaction quantitatively and measured the rate of evolution of oxygen volumetrically. Some work done by Troué on the same salt yielded like results.

The Permanganate.

The potassium permanganate solution: It has already been stated that the solution of this substance in the presence of the ferrous ions and ceric ions in the standard solution

Permanganate. The preparation of the solution to be electrolyzed was as follows: large Taxon evaporating dishes of nine to ten litres capacity were filled with distilled water which was heated nearly to boiling then was added the crystallized potassium permanganate a little over forty grams per litre of water. Constant stirring insured the solution of ~~the salt~~ ~~the solution~~ the solution was filtered very carefully to remove the manganese dioxide the presence of which deco causes ~~an oxidation which is not~~ ~~the same as the~~ filtration the solution was passed or rather drawn by means of the ordinary filter-pump.

series of asbestos filters filled upon
perforated porcelain disks (Witt plates)
which had been placed in the so-
called North primary. These filters
were joined in a series by means of
copper stoppers.

For convenience in calculating the
yield of acid by each cell and the
purity of the acid obtained, it was
desirable to have the permanganate
solution of given strength: about
0.01 milligrams per cubic centimeter
of solution. The filtered solution of
potassium permanganate was then
diluted with distilled water to
of carefully prepared potassium tetrox-
alate and then diluted so as to be

of the potassium permanganate solution it was subjected to electrolysis and the solution was then concentrated to obtain a concentrated solution of acid obtained and then whether or not the acid contained any alkali, any undecomposed potassium permanganate.

The strength of the solution of the acid was easily determined by titration with weighed portions of potassium tetroxalate. For the detection of the permanganate if there was any in the solution, there were two methods available the chief difference between them being the decolorizing agent. One method consisted in measuring the volume of the solution required to decolorize a certain volume of the solution of potassium tetroxalate.

ganic acid the strength of which has
 been accurately determined. Then in a
 another beaker measure a volume of
 potassium permanganate exactly the equivalent
 of the permanganic acid in the first
 beaker. Now to each beaker add the
 same volume of sulphuric acid, a
 quantity more than equivalent to the
 potassium and the manganese in
 the second beaker. After adding
 just to the point of decolorization
 hydrogen peroxide which has been
 neutralized with zinc oxide. Then
 with ammoniac solution of known
 strength for the excess of sulphuric
 acid in each of the two beakers.
 It is evident that by finding with
 the known ammonia solution ^{of known concentration}

potassium permanganate which was in the permanganic acid.

The other possible method for this determination

of ~~known~~ permanganic acid and known potassium permanganate solution, are

the following: ~~the first method is the most accurate~~
time to each beaker and the reduction of the permanganic acid or the permanganate solution by means of oxalic acid. The titration with permanganate as before. This method has some advantages over the first: the hydrogen peroxide in the first method interferes with the indicator, that is if methyl orange is used. If oxalic ~~acid~~ strength be used it renders unnecessary for this particular

The standardization of either the permanganic acid or the potassium permanganate for by measuring into beakers equal volumes of ~~the same~~ ~~acid~~ ~~and~~ ~~the~~ ~~permanganic~~ ~~acid~~ ~~and~~ ~~the~~ ~~potassium~~ ~~permanganate~~ ~~we~~ ~~have~~ ~~only~~ ~~the~~ ~~same~~ ~~volume~~ ~~of~~ ~~the~~ ~~acid~~. Strictly speaking in

standardizing the permanganic acid or potassium permanganate we do not titrate to color, but add an extra drop of oxalic acid to leave a colorless solution.

Both of these methods were tried and the amount of permanganate found was so small that there was no fear of its interfering with the later stages of the analysis.

the preparation of the salts.

The method of preparing the salts originally chosen was to treat the purified carbonates of the metals with the permanganic acid. However, the permanganic acid was so impure that it was necessary to purify it. So it seemed advisable to take the purest oxides of the metals that could be obtained and treat them with the acid - reacting in the presence of sulphuric acid for the decomposition of the water of hydration. It was finally found that about three hundred grams of permanganic acid was in abundance at the disposal of each of the three metals whose permanganates were proposed to study.

of acid inversely proportional to the mol.
... of it. ...
I hoped to prepare approximately an
the same weight of each salt.

The result of the calculations is to
this division of the acids:

ZnO	"	"	303.14	"	33.00%

So the Magnesium Oxide was to have
...
160. grams " " " Cadmium Oxide

148.
148.
149.5 The weight of oxide to be
used was cal in each case was
calculated and care taken to
have a considerable excess.

The three solutions were allowed to
stand for 24 hours or thereabouts

negative. During the time it took to
run the temperature of the solution
when it was thought the reactions
were completed they were followed down
water as already described to the
filtration of the platinum form
etc.

The evaporation to crystallization of the
solutions was a long and tedious pro-
cess it was in each case done in a
water bath but in spite of the paper
screens kept over the evaporating
surface the loss in the atmosphere
brought the composition in each
one to such a point that other means had
to be adopted. It may as well be
said that a repetition of this evap-
orating on water bath would probably
have given some better results.

it is under the action of the same
 forces with the decomposition they
 pass right to such case if the
 reaction is not immediately observed
 with dust particles.

Due to the rapid decomposition on the
 walls ^{on account of the abnormal amount of oxidizable material} ~~the~~ ^{in the air at the time} the reaction was carried
 out at a low temperature $30^{\circ}-35^{\circ}$.

To this end a ground glass plate was
 placed on the top of an ordinary air
 bath and the reaction was carried out
 in a glass vessel placed on it and covered with an
 open neck bell-jar. Into the neck of
 the bell jar was fitted a three hole
 rubber stopper. Into one hole was
 a thermometer the bulb of which
 was immersed in the reaction
 The second hole contained a

1
tube the end reached with about a
centimeter of the solution at the bottom
the other end connected by means of
rubber tubing with a calcium chloride
tower, filled with calcium chloride
solution. The third hole was fitted
with a glass stopper. The
Bunsen burner heated the bath and
solution: the pump sucked air
and pieces of, by the calcium chloride over
the solution in this way the water
was removed as fast as formed
thus by hastening the evaporation
by keeping dry the air above the
solution. The purpose
of these salts to form supersaturated
solutions at a temperature slightly
above the ordinary heat.

in each case. At the close of each day's
evaporation it was necessary to filter
the solution so as to remove the
manganese dioxide formed during
the day. It has already been pointed
out that the presence of manganese
dioxide in a solution of potassium
permanganate hastens the decompo-
sition of that salt. It is probably
the ^{action of the dioxide on the salt} formation of more complex
~~compounds of manganese~~ compounds of manganese.

It was found to be the case with
the other salts investigated so it was
necessary to filter the solutions at
the close of each day. To return to
the supersaturation of the solutions
above referred to; when a volume
of the solution had been evaporated
down from time to time

about one tenth of that volume. When
sufficient amount of acid had been added
to run around the solution was
so much supersaturated with sugar
allize in the siphon and on the
filter during the process of fil-
tration. A thermometer in the siphon
had not fallen more than fifteen
degrees when the precipitation and
clogging of the filter took place it
was necessary to heat the siphon
and for a while and keep them ^{open} until
until the filtration was com-
pleted. Having brought the solu-
tion to a syrupy consistency it
was placed under a steam bath
all night with another degree
concentrated sulfuric
acid. And allowed to stand for

... days, and then the crystalliza-
tion began. In each case the first
crystals to be obtained were found
by analysis to be the potassium
permanganate which was in the
acid.

The decomposition of the
solution was very rapid, and the
evolution of oxygen was very rapid.
When the solution was heated on the
water bath, the decomposition was
so rapid that it was difficult to
keep the water bath under the same condi-
tions. So rapid was the evolution of
oxygen by this decomposition that
the room was almost uninhabitable
the ozone attacking and irritating
the throats of the workers in the
room. At a lower temperature

protected from the dust by the bell jar
the rate of decomposition was not
nearly so great but was still greater
than that at the higher water
vapor pressure.

Having obtained in long cactus needles
crystals of the salt as desired
sired to get some of them air-dry
preparatory to the analysis of the
salt. A few grams in a weighing tube
were placed under the bell jar
and the mouth of the tube
with filter paper to exclude dust
particles and still allow free
circulation of the air. The tube

was placed under the bell jar
and the mouth of the tube
with filter paper to exclude dust
particles and still allow free
circulation of the air. The tube

the microscopic condition of the

Insert what is written on enclosed slip

tion. The maximum gain in
^

weight, on the most humid day was
39 milligrams over the weight on
a very dry day. 3.019^{86} grams of
the salt were used in this determin-
ation, so the maximum per cent
ex change in weight is a little
more than one and one ^{quarter} per-
cent. The deliquescence of the salt
in moist air made difficult the
accurate analysis of the salt.

It was afterwards found that if
kept in a porous porcelain dish
the deliquescence was reduced to
a minimum so the plan of the
to absorb all the moisture without
losing away the water by evapora-
tion. Unfortunately this fact of the
Comparative constancy in weight of
the salt kept in touch with the

was not considered until the weighing
was nearly completed.

~~weight of the substance that~~

In order to find how the salt would
conduct itself when exposed to the dehy-
drating action of sulphuric acid, a
few grams of it in an unstoppered
weighing bottle were placed in a
desiccator over this liquid.

The following are the results recorded

March 30th tube alone 21.0353 gr
Weight of salt used 3.0220 gr
Total salt 24.0573

April 2 nd	"	"	"	27.0476
April 17 th	"	"	"	27.0206
May 26 th	"	"	"	26.9392
May 26 th	"	"	"	26.9265

After each weighing in this and other
water determinations

During the salt was well shaken in order
to expose more surface to the
conditions. From the results given it will
be seen that 3.022 grams of the salt
lost during a period of eight weeks
1.338 grams or 44.3% ⁱⁿ of its weight.

Now, as will be shown later, this salt
~~is not stable with an atmosphere of water~~
~~of relatively low humidity~~ ^{the weight of salt & this loss corresponds to}
have not enough data to conclude

how many of these molecules it
would eventually give up under
conditions it is in contact with
water in the air. It is noted that
cause the loss in percentage of loss
in weight is several times as great
as the percentage of maximum
variation in weight when exposed
to the air alone. loss corresponds

ing that the salt will eventually give up
the molecule of water of crystallization
though that seems highly probable and it
is quite possible that more than one mole-
cule would be lost on account of the
dehydrating action of the sulphuric
acid. 250°C. the water of crystallization is lost. The acid is already present in the crystalline salt.

Stability over Calcium Chloride
As to the ^{stability of the} stability of this salt over
sulphuric acid its stability when
subjected to the dehydrating ^{action} of calcium
chloride was also taken up. The method
of measuring the determination was
nearly the same using calcium
chloride instead of sulphuric acid.
The following are the results
made.

March 20th 1911
Salt used 3.4722 grams. Product 2.0
2nd 3.1

May 26th " " " 3:0000

in this case 3.122 grams of the salt
in the same length of time lost only
.0536 grams in weight or 2.1% per cent.
This is but little over half the percent-
age of loss over the sulphuric acid
and this is so due to the fact that
the reaction in weight of the salt
is far in excess of the one that is known
for doubt as to its being water of
crystallization that is given.

Determination of Manganic Feils
The determination of the manganic
Feils the method used was in brief
the following: A portion of the
sample was dissolved in water
and a little sulphuric acid was added.

Now into the beaker containing this solution
is weighed such a quantity of potas-
sium chlorate in the dry form
by which it is in more than excess
to saturate the hydrogen peroxide. The chlor-
ate was used purified by several
recrystallizations and the ^{loss of} water of crys-
tallization due to mechanical enclosure
was eliminated as far as possible by
recrystallizing the salt rapidly 10-15
times under vacuum. After adding
the excess of chlorate the solution
is warmed and becomes colorless.
Potassium perchlorate carefully
dried by CaCl_2 is now weighed in its
color. The equivalent of the excess
present in chlorate can be calculated
and was subtracted from the total
weight of potassium perchlorate.

The difference was the equivalent in
 titroxalate of MnO_4 in the salt weighed
 out. The determination was made by
 the method of titration of the
 solution of water of crystallization
 in the salt. The result was
 63.70. The method of determining the weight of
 the water of crystallization was as follows:

Weight of water of crystallization

63.70

Weight of water of crystallization for 6 mols
 of water of crystallization

64.264

Error (partly due to hygroscopic conditions)

0.564

Determination of Magnesium

The analysis of the magnesium carbonate
 for magnesium followed the
 determination of the permanganic acid.
 To a gram of the salt weighed into
 a beaker was added hydrochloric acid.

which gave negative tests for nonvolatile substances in solution. Upon the further addition of a few drops of sulphuric acid the solution became clear and colorless and contained the soluble iron, manganese and magnesium. This solution was then added to a solution of ammonium sulphide prepared by adding a few drops of concentrated ammonia with purified hydrogen sulphide and then adding to this an equal volume of the same ammonia. The addition of the ammonium sulphide to the solution containing the two sulphates caused the precipitation of all the manganese as sulphide. This was carefully filtered off by means of an asbestos filter. The filtrate contained only the magnesium.

sulphate and sulphide. This was evaporated to a small bulk with on the water bath and to it added gradually a solution containing ammonium phosphate and ammonium Chloride.

The white precipitate of magnesium ammonium phosphate separated, which was filtered, dried and ignited to constant weight, as magnesium pyro-phosphate. The result agreed fairly well with the theoretical.

Magnesium found	6.40%
Theoretical for 46 mols water	6.55
Error	

The direct determination of water of crystallization involved no loss.

whatever and yielded quite good results
A piece of ordinary combustion tub-
ing placed on the furnace was
filled with a Calcium Chloride
tower at one end for the purpose
of drying the air entering the tube.
The other end was attached to a
weighed Calcium Chloride U-tube
and to this in turn a Marchand
tube filled with calcium chloride
to protect the weighed tube from
moisture. The whole
system by means of the later
bump in a position where it was
weighed from a half a gram to
a gram of the magnesium bar
magnesium carbonate. After the
tube had been heated to red heat
the magnesium was weighed.

was placed in the tube which was then gradually heated. During the heating air was taken through by the suction pump and the water collected in the weighed U tube.

Water found	24.8%
Theoretical for air molecules	29.10
	.08%

Analysis of the magnesium salt
A determination of the solubility of
the salt at 25° was made in the
following way: a solution containing
more of the salt than it could possibly
dissolve was allowed to stand
for several weeks in a place of
nearly constant temperature. It was

stirred from time to time. After the
determination was made it was

volume was extracted and diluted in a graduated flask to 100 c.c. This was allowed to stand until the solution was homogeneous - the homogeneity being insured by shaking from time to time. This solution was titrated against previously standardized ferric acid. A series of two titrations showed 10 c.c. of the oxalic acid solution equivalent to 13.07 c.c. of the salt solution (diluted to 100 c.c.). The oxalic acid contained 47.61 milligrams of the acid per cubic centimeter of the solution. So 47.61 milligrams acid were equivalent to thirteen hundredths of one of the salt in the volume taken. Now since one gram of oxalic acid reduces 502.1 milligrams of potassium

5021 grams of magnesium carbonate that using the ratio of the molecular weights, $\frac{370.4}{158.14} \times 5021 = 1.173 \text{ gms}$

If one gram of the acid reduces 1.173 grams of the salt it is a matter of proportion to calculate the weight of salt reduced by 470 milligrams of the acid. From this part in 150 cc of the 100 cc solution it is simple to calculate the weight of salt in the whole flask. The total weight of salt taken out divided by the volume of the solution that was extracted will give the weight of salt per cubic centimeter of the solution. Total weight of salt found was 4.218 grams and this divided by 151 the volume

in cubic centimeters taken will be the weight of the magnesium salt per cubic centimeter of saturated solution. In a saturated solution of magnesium permanganate decomposes on heating especially in the presence of an organic substance and since it decomposes in a way analogous to the decomposition of potassium permanganate

$MgMnO_4 \rightarrow MgO + MnO_2 + O_2$
it must be that it has formed
previously above the molecular weight
being 370 it is given when decom-
position about 21.6% of oxygen.
In a saturated solution the available
oxygen will be 21.6% of 2.711 grams
or 602 milligrams per cubic cen-
timeter of solution.

with such a solution is easily demon-
strated by pouring a little of it into
a beaker containing glycerol which
has been warmed. The reaction is
quite violent and the supersaturated
solution is decomposed with gas
evolution. On one occasion a few drops
of the supersaturated solution ^{dropped} fell
on the desk and I removed them
with a piece of dry filter paper.
In doing so I rubbed the desk
quite energetically to remove all
the stain. Then I threw the paper
into the waste jar. In a few
moments I saw smoke coming
from the jar and looked to find
the piece of filter paper burning.

It is quite probable that the smoke
and complete oxidation of the

manganate compounds by magnesium. The
manganate will prove a basis for the
analysis of acid compounds. In
fact some work on this problem
has been in progress in this labora-
tory during the past few months.

~~The purpose of this study is to determine the properties of the magnesium manganate and to compare them with those of the other manganates.~~
It will be of interest to compare in a
general way the properties of magne-
sium permanganate and see how they
agree with what we should have ex-
pected of a salt of magnesium and
of permanganic acid.

The magnesium salt especially in
the presence of water shows a ten-
dency to decompose at moderate
heat. All permanganates when heated
have the same behavior and give

oxygen is one of the products of decomposition. We might then have anticipated the rapid decomposition of a solution of the salt on evaporation and the copious evolution of oxygen which we have seen should come off as soon

as I have been mentioned that upon evaporation of the most concentrated solution under the bell jar a bubble rises above the water which was being drawn out of the ^{cell jar} solution by the pump. This reaction could not be studied quantitatively but may probably be represented by the equations



and this acid in turn, breaks down thus



As regards water of crystallization the fact that it crystallizes with six molecules of water is not surprising, as metals can be supposed to have any tendency toward crystallizing with a certain number of molecules of water. The following compounds show the large proportion of the primary salts of magnesium which carry six molecules of water.

$MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$

$MgH_2PO_4 \cdot 6H_2O$, $MgH_2PO_4 \cdot 6H_2O$, $MgH_2PO_4 \cdot 6H_2O$

$MgH_2PO_4 \cdot 6H_2O$, $MgH_2PO_4 \cdot 6H_2O$, $MgH_2PO_4 \cdot 6H_2O$

$MgBr_2 \cdot 6H_2O$ (or 10, dependent on conditions)

$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot 6H_2O$

$MgCO_3 \cdot 3H_2O$,

From the stand-point of permanganic acid we might consider the magnesium compound a salt of H_2MgO_4 .

The Zinc Experiment
The decomposition of the solution of the
has already been given
Zinc salt both on the water bath and
at a lower temperature under the bell-
jar was accompanied by much less
decomposition than was found in
the case of the magnesium perchlorate
etc. It is believed that under the
most favorable conditions it requires
heat in the atmosphere the zinc salt
would prove fairly stable on heating
alone. In fact the decomposition
under the bell jar was not very
great and would doubtless have been
even less had the solution not ac-
tually decomposed due to the
loss of oxygen or the escape
of the ozone was indicated by the de-
composition of the salt at 100°C.

Notice though no test was applied
to prove its sterility. The tendency
to super-saturation referred to in the
case of the magnesium salt was also
promoted by this salt. Under a glass
bell jar with sulphuric acid the well
formed crystals were obtained
in what seemed to be hexagonal habit
capped by pyramidal form. These
were larger and more regular in form
than those of the magnesium salt
but none were obtained of which it
was thought satisfactory goniometric
measurement could be made.

In the air the constancy of weight
was ^{determined} measured as already described
and the recorded weights are as
follows:

March 13th. Weight of tube alone 29.864

" " " " Salt taken 4.973

March 14th " " " " " 34.835

March 15th " " " " " 34.834

March 16th " " " " " 34.831

March 21st " " " " " 34.830

4.973 grams of the salt showed a maximum change in weight due to atmospheric conditions, of six milligrams the equivalent of about twelve hundredths of one per cent. On a barometer reading plate this variation was reduced to a minimum.

Stability over the plate

The determination of the stability of this salt under the laboratory conditions

of sulphuric acid was made ready in
the same laboratory was made
with the magnesium salt. These are
the recorded weighings

March 16th Weight of tube alone 24.2425

" " " " " salt used 3.3655

" " " " " residue 5080

March 19th " " " " " 27.5653

March 20th " " " " " 27.5620

March 27th " " " " " 27.5011

April 12th " " " " " 27.4504

April 17th " " " " " 27.3330

May 24th " " " " " 27.0092

May 26th " " " " " 27.0085

From these results we see that the
total loss of weight was 3.3655 grams
about nine weeks of 3.3655 grams of
the salt was 5.925 grams representing
7.81 per cent. The maximum is...

in weight of the salt due to atmospheric
 loss but $\frac{12}{100}$ of one per cent so this
 change is ~~probably~~ ^{or near} ~~the same~~ ^{the same} as the loss of
 water on crystallization to the sul-
 phuric acid, & much more constant
 in the study of this loss of water
 would be necessary to determine how
 many molecules would be given up
 by the salt to the acid.

Stability over Calcium Chloride

This was a repetition with the same
 set of the conditions of the determina-
 tion described for the magnesium
 salt. The recorded weighings were:

March 16th Weight of flask 22.9704

Net salt 2.702

"tube + salt 25.5653 "

March 19th " " " " 25.3500 "

March 20th. Weight of tube + salt 25.2462

March 27th " " " " 25.2543

April 2nd " " " " 25.2575

April 17th " " " " 25.1120

May 24th " " " " 24.9195

May 26th " " " " 24.9091

The total loss in weight during a period of about nine weeks was 2.3371 grams of the salt taken. This is 16.2% in weight, showing necessarily a loss of water of crystallization since the maximum variation in the air was $\frac{12}{100}$ of one percent.

Determination of Permanganate
The method of making the salt (see note at the end for MnO₂) was exactly the same as that described on page 28 et seq. for the same.

with the magnesium formate
the results clearly indicate the mole
ratio of water of crystallization

MnO₄ found

57.70%

MnO₄ required by theory for 6 mols water of crys 57.85

Error

.15%

Determination of the zinc

Weight of 1 gram of the salt was weighed
into a beaker and reduced with the
hydrogen peroxide containing no
non-volatile ^{substance} matter. Dilute ac-
etic ^{or hydrochloric} acid was added just in sufficient
quantity to convert both the manga-
nese and zinc into sulphates ^{of} com-
ing salts and make the solution
slightly acid. To this solution acetic
acid was added until it possessed
the strong odor of that acid, then
codium or barium acetate was

to take all the mineral acid present and convert the manganese and zinc into acetates. The sulphide of manganese is quite soluble in formic acid while the sulphide of zinc is not. So this was the basis of separation. Hydrogen sulphide was passed in to saturation and the milky white precipitate of zinc sulphide immediately came out. In most cases it was accompanied by a little manganese sulphide. Where upon both of them as had to be redissolved in mineral acid and the precipitation of the zinc sulphide resumed. That was carefully filtered ^{separated} ~~separated~~ in hydrochloric acid and ^{the solution} ~~separated~~ evaporated to small volume on the water bath.

followed solution of pure sodium carbon-
 ate was then added drop by drop to
 the boiling solution of zinc chloride
 when the latter became quite alkaline
 the addition of the sodium
 carbonate was discontinued but
 not the boiling of the ^{solution of the} zinc salt.
 Soluble zinc salts are precipitated
 by sodium or potassium carbonate
 but are somewhat soluble in the
 precipitate. The object of the continued
 boiling was to prevent this re-
 solution of the zinc salt. The precipi-
 tated carbonate was boiled several
 times with water, which was decanted
~~off~~ through the filter upon which
 the precipitate was to be collected,
 when it was thought that all the
 sodium chloride had been removed.

in this way and all the solution from
cells has been recovered into the
beaker. The precipitate was collected
on the filter and dried in an
air bath. It was then counted in
a weighed porcelain crucible.

from 1000

1000

Recovery in an aliquot of 1000
from

Recovery of cells of *Staphylococcus*
About half a gram of the cells was
weighed into a porcelain boat. The
boat was sealed in the combustion
tube and heated as previously described.
Page 52 is of the results obtained
which agree quite well with that required
by theory for an molecular weight
of crystallization.

from 1000

from 1000

A known volume of a saturated solution of the salt was diluted to the mark in a graduated 100 cc flask and this solution 15.1 cc was well mixed and then the solution was titrated against standard oxalic acid solution.

10 cc of the oxalic acid 47.61 mg were equivalent to 16.66 of the permanganate. Hence 60 cc. of the Oxalic \approx 100 cc of the permanganate or the whole solution
 $0.4761 \times 60 = 2.8566$ grams of oxalic. Now

grams of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ then
grams of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ then
 $2.8566 \approx 3.7307$ grams of this salt. But 15.1 cc was the volume of the solution taken so $\frac{3.7307}{15.1} = 2.479$ represents the salt contained in one cc. of the solution.

...at that temperature (22°)
The saturated solution of zinc permanganate although an unusually powerful oxidizing agent does not prove as effective for this purpose as does the saturated magnesium salt solution. In the first place the zinc salt is not quite so soluble as that of magnesium and in second place it is more stable & does not seem to yield up as the other salt does

General Remarks on the Zinc Salt

The crystals of the zinc permanganate resemble very closely those of the magnesium salt. ^{show} crystals were larger than those from the magnesium salt.

Zinc salts in solution resist decomposition at moderate heat more than those of magnesium. As far as they can be oxidized to permanganate in process but is common

some extent on heating it is not surprising then but rather to be expected that the zinc permanganate although it decomposes to some extent upon evaporation of its solution loses so much less than the magnesium salt.

As to water of crystallization there are no facts that seem to indicate any tendency on the part of zinc compounds in general to crystallize with a particular number of molecules of water of crystallization being a typical metal phase and possessing many properties in common with manganese we might represent the formula of the salt as a normal one with the normal permanganate.

masses is analogous to the magnesium salt. $\left\{ \begin{matrix} \text{Mg} \\ \text{Mg} \\ \text{Mg} \\ \text{Mg} \\ \text{Mg} \\ \text{Mg} \\ \text{Mg} \end{matrix} \right\}$ etc. In a matter of fact it is contained in molecules of water of crystallization and this furnished indications as to velocity obtained by analysis.

The Cadmium Formate.

When a solution of the salt was placed in the ultrasonic apparatus, upon incorporation in water bath and at low temperature under the influence of the ^{ultrasonic} waves the magnesium salt proved to be more stable than either of the two salts already described. In fact the decomposition was very slight indeed and it is my belief that under most favorable conditions as regards time particles in the air, this salt would

scarcely decompose to an appreciable extent during a long exposure. The crystals were obtained with less difficulty than those of either of the other two salts. It has been stated that the crystallizing force of the zinc salt was greater than that exhibited by the magnesium salt. The Cadmium salt decomposes either of these and even a concentrated solution of it allowed to stand under a bell jar with sulphuric acid for three or four months. There would doubtless be obtained large and well developed crystals provided the temperature of the solution was kept constant. When exposed to the air the crystals

is shown by the following results

March 16. Weight of tube alone 34.1800

" " " " salt used 6.3508

" " " " tube + salt $\overline{40.5308}$

March 19th " " " " 40.5306

March 20th " " " " 40.5362

March 21st " " " " 40.5306

March 22 " " " " 40.5303

The maximum variation in the weight
of 6.3508 grams was .0059 grams
about $\frac{1}{100}$ of the amount

Stability over sulphuric acid

For the stability over sulphuric acid
the determination was made in a
very accurate way the following are
the weighings

March 16th Weight of tube alone 34.1800

" " " " salt used 6.3508

March 5th	Weight of Salt	39.7702
19th	" " " "	39.7711
20th	" " " "	39.7711
27th	" " " "	39.7722
April 2nd	" " " "	39.6782
April 17th	" " " "	39.6831
May 24th	" " " "	39.2890
May 26th	" " " "	39.2626

The entire loss in weight during about nine weeks by 5.4829 grams of the salt was .5256 grams or 9.03 per cent. The maximum change in weight in the one week was one per cent. As this salt also was one of the samples which was used in the experiment it is evident that it was not as stable as the others.

The following are the results

recorded in the study of the stability
of this salt over Calcium Chloride
March 16th. Weight of tube alone 48.7478

" " " " Salt used 44.528

" " " " Tube + salt 48.7490

" 19th " " " " 48.7493

" 20th " " " " 48.1830

" 27th " " " " 48.1360

April 2nd " " " " 48.0943

April 17th " " " " 48.0040

May 24th " " " " 47.7828

May 26th " " " " 47.6711

The water loss being 5229 grams
by 44.528 grams of the salt. Assuming
these figures were correct on 19th as that.
Knowing the comparative constancy
of the weight of this salt in the
air we see it loses weight of approx-
imately 10 Calcium Chloride. Only
the water which is absorbed by the salt + that of the air which is

Determination of Iron in Organic Acids

The method for the determination of Iron in the other two acids was the one used in this case. A small portion of the salt of potassium bitartrate in the same beaker were treated with water and dilute oxalic acid. Standard potassium permanganate titrated in solution and the excess of bitartrate solution. The results were indicative of 1 molecule of water of crystallization.

Found

51.84%

Required by theory for 6 molecules of water 51.88%

Determination of the Calcium

For this determination it was necessary to precipitate the calcium

but wash it as such. To this was
about a gram of the salt was added
into a beaker. Hydrogen peroxide
was added and then just enough
hydrochloric^{acid} to complete the dissolu-
tion of the solution. This
was poured into a saturated water
solution of hydrogen sulphide.
The water solution of the gas was
used to further dilute any free
mineral acids in the solution.
The cadmium was precipitated
as the lemon yellow sulphide.
The filter to be used in this de-
termination was dried to con-
stant weight at 100° in a
weighing bottle. The precipitate
was collected on this filter dried
in the air bath at 100° to a

Calcium sulfate

Calcium found	23.11%
Theoretical for 6 molecules of water	26.51%
	<hr/>
	.34%

Determination of Water of Crystallization
The method used for the determination of water of crystallization in the other two salts was repeated in this and yielded results agreeing with six molecules.

Per cent of water found	23.43%
Per cent required for six molecules	26.55%
	<hr/>
	.15%

The solubility of the Calcium salt
15 cubic centimeters of a saturated solution prepared as previously described was diluted to 100 cc. in a graduated flask. By titration against the mercuric nit solution

milligrams per cubic it was found that
 15 cubic centimeters of the oxalic were
 equivalent 25.55 cubic centimeters of the
 permanganate solution. From which
 10 cubic centimeters of the oxalic
 are equivalent to 16.7 cubic centimeters of the permanganate.
 Now 100 cc. the whole permanganate
 solution would be 167 cc. ^{5.75} which
 applied by ten the number of cubic
 centimeters of the oxalic used approx-
 imate to all the permanganate.

$$50.75 \times .4761 = 2.737 \text{ gms } 2.737 \times 1.45 \left(\frac{458.44}{1522} \times .5021 \right) \div 1.51 (20\%) = 2.6275 \text{ gms}$$

Properties. Potassium permanganate is a dark black
 crystalline substance in the form of small
 of its solutions at moderate heat
 resembles the other salts of that metal
 but it is a powerful oxidizing agent and has
 a tendency to crystallize with
 water.

molecules of water of crystallization
 but in the case of the zinc salt
 magnesium we may also consider the
 potassium permanganate to be the
 normal salt of the so-called nor-
 mal permanganic acid. Its for-
 mula might then be represented
 thus



Comparing the three salts
 having established the compo-
 sition of these three salts and
 brought out certain facts common
 to all of them or peculiar to one
 it may prove of interest to bring
 together the established facts

compare them, see if we should have anticipated any of the facts or if any one of them has properties that we should have had no reason to expect. This comparison has now entered in to some extent already but there are I think other points of interest that have not been mentioned.

Having established experimentally the identity of the magnesium permanganate and having proved by analysis the formula to be $MgMnO_4 \cdot 6H_2O$

Mg	64.0
MnO ₂	63.70
H ₂ O	29.18
	<hr/> 99.38

The zinc permanganate has been shown to have the formula $ZnMnO_4 \cdot 6H_2O$ by the following

analysis

30	13 50
MnO ₂	57 70
H ₂ O	26 18
	<hr/> 97 38

The Cadmium permanganate has been analyzed and shown to have the formula $\text{Cd}(\text{MnO}_4)_2 \cdot 6\text{H}_2\text{O}$

Cd	24.12
MnO ₂	51 89
H ₂ O	23 43
	<hr/> 99 44

In the preparation of the solutions of these three salts to crystallization the process in each case was begun on the water bath and afterward continued at lower temperatures in a water bath. The

It was both of these materials at
first rapid decomposition when
the container was opened but it
came the zinc dust which was
somewhat more stable decomposed
slightly and seemed to yield no
ozone. The Barium permanent
proved to be the most stable of the
three and as already stated would
doubtless be evaporated in filtered
air without appreciable decomposi-
tion. It is interesting to notice
this variation of stability under
certain conditions and to observe
the agreement with the periodicity
of the elements. Magnesium has the
lowest atomic weight ^{common} zinc the
highest and zinc about the mean
between the other two.

Would rather expect them to possess
in varying degree a property common
to all of them, the variation being
as indicated by the atomic
As regards the ~~the~~ crystallizing form
of these three salts the magnesium
seems to possess it in the least de-
gree for it was impossible to ob-
tain crystals of ^{any} ~~any~~ size from this
salt. Although it would doubtless
yield better results were it allowed
to stand longer under a bell jar
with the desiccating agent the tem-
perature being kept low.

The zinc salt yielded crystals much
better developed than those obtained
from the magnesium salt and the
chromium possesses to the highest
degree of any of them the

During the time that the solution was being
the partially saturated solution as a factor
in crystallizing from solution the
marked tendency to "creep" along
the sides of the dish was shown
by the magnesium salt. One morn-
ing upon examining the solution
that had been standing for several
days it was found that the salt
crystals had "crept" about twenty
millimeters up the walls of the
containing vessels and were pro-
jecting about the same distance
over the sides of the vessel. It
was not at all unusual in the
crystallization of this salt to find
on the glass plate near the dish
containing the solution a deposit
of the salt that had "crept" up.

of the salt the tendency to trap was
not nearly so marked in the case of
the zinc salt and the Calcium
salt possesses it in the least degree.
As regards order of crystallization
all three of these salts ^{crystallize with} carry the
same number of molecules and
there is no room for preference.
but in as much as order of crys-
tallization is in a way a constant
of the molecule we should not
have expected a periodic variation.
All three of these salts at high
temperatures having lost their order
of crystallization giving up the
volatile anhydride of the peroxide
peric acid, Mn_2O_3 . Magnesium
does this more readily for it has
already been mentioned.

a small quantity of the sulphur
dioxide the evaporation of its solution
under the bell-jar. In fact during
the evaporation on the water-bath
which had to be discontinued on
account of the evolution of
oxygen (no ozone) the sulphur
fumes rising from the evaporating
surface were noticed. There were
it is believed mostly those that
were not collected and only
the loss of weight in the air is
dependent on the humidity and so far
have seen for the magnesium salt
one and one fourth per cent for the iron
salt about $\frac{1}{2}$ of one per cent and for
the cadmium salt $\frac{1}{10}$ of one per cent
for the magnesium salt while the
greatest tendency to deliquesce

and the calcium salt of tartaric
acid. The magnesium salt of tartaric
acid lost during eight weeks 4.43 per
cent in weight almost the equivalent
of one molecule ^{of water} for six molecules con-
stitute 24.10 per cent of the salt
The zinc salt lost during nine weeks
17.81 per cent in weight. corresponding
to about nearly four molecules of water
of hydration as the six found
constitute 35.249 per cent of the crystal
hydrate salt The calcium salt of
tartaric acid lost 4.03 per cent
in weight during nine weeks.
These results are not quite compa-
rable for this reason. The salts
do not lose water at the same
rate from day to day and the
determinations were for nine

In two of them and eight cases in the other the weighings were not made daily in the desiccator would be less difficult.

For the same reason the loss of weight over Calcium Chloride of the three salts are not comparable - these were for Magnesium zinc and barium permanganates respectively 2.47% 6.42% 11.74 per cent. From these data we see that there was not a great relative difference between the dehydrating action of these two agents sulphuric acid and Calcium Chloride on these salts.

It was noticed that these salts after having stood in the desiccator on the dehydrating agent rapidly re-gain weight on exposure to air.

All of these salts on standing decompose slightly and the crystals become covered with manganese dioxide which imparts to them a greenish purple instead of the original deep purple color.

Magnesium and Cadmium Salts of the higher oxygen acids of the Manganese group

It is worthy of note that the Magnesium and Cadmium salts of the highest oxygen acids of the halogens Chlorine Bromine and Iodine which fall in ^{the} same group with manganese are all with a few exceptions notably Cadmium Periodate very soluble in water some deliquescent and some ~~are~~ ^{forming} crystals of hydration.

Biographical Sketch

Harold Chaubless was born in Selma, Alabama December the fourth of the hundred and seventy two. His early education was received in the schools of that city and by private instruction. In 1890 he entered the Virginia Military Institute where he was graduated in 1894. He became a graduate student in Chemistry, Biology and Physics in the Johns Hopkins University in October 1895 and continues as such for two consecutive years. After an absence of two years during one of which he was Scholastic Fellow at ^{Yale} ~~Yale~~ and received the degree of Master of Science, he returns to the Johns Hopkins University in October 1899. He commences his course for the





